The Band Spectrum Associated with Helium.

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A very significant addition to our knowledge of the nature of band spectra has been made by Prof. Fowler,* who has lately described the results of his examination of the band spectrum found in connection with helium and hydrogen, and believed to be a spectrum of helium. For Halm† has maintained that the formulæ which must be used to represent line and band spectra are intimately associated, and, in fact, spectroscopists have been generally inclined to suspect that the laws of line spectra have some counterpart in band spectra also. Fowler has taken the first step in the elucidation of this connection by showing that the universal constant of Rydberg belongs to this individual band spectrum, which contains two series of double "heads" arranged essentially in the same manner as the lines in a series spectrum.

One feature, however, of these double "heads" or doublets appears at first sight to differentiate them from the doublets found in line spectra, and one purpose of this paper is to show that the difference in character is only apparent, and that the formal analogy with line spectra extends very far. In ordinary Diffuse or Sharp series of doublets, the intervals between the components, when expressed in wave numbers, are constant, whereas in a Principal series the intervals rapidly become smaller, and vanish at the limit of the series. The intervals decrease, moreover, in a very regular manner. In the band-doublets discussed by Fowler, although the intervals decrease as the series proceed towards their limits, the decrease is not very regular, as shown by the differences, and the intervals do not obviously vanish at the limits. Without a very precise arrangement in series, it is not possible to judge of their limiting behaviour.

Fowler has shown that the less refrangible components can be arranged in series of a very ordinary simple form, that of Rydberg being almost sufficient. But the more refrangible components cannot be arranged in a satisfactory manner, even in a Hicks series. They are, in fact, an example of a phenomenon not unknown in line spectra, where lines which obviously belong to a series cannot be fitted in a satisfactory way into the usual formulæ, because those formulæ do not, in these individual cases, converge with sufficient rapidity.

* 'Roy. Soc. Proc.,' A, vol. 91, p. 208 (1915).
† 'Roy. Soc. Edin. Trans.,' vol. 41 (1906).

It will become apparent in the paper that this approximate superposition of two series with the same limit, but with very different modes of convergence among their coefficients, is the cause of the unusual character of the doublet separations. Fowler has already suggested that these two phenomena are related, but has not carried the calculations to the extreme point which can decide whether the separations are of a new type or not.

Two series of doublets have been noticed. In the first series, three have been measured with some accuracy, and six others in a more approximate manner. In the second series, there are four members, all well measured, and this series may be most conveniently discussed first. Its wave numbers, expressed in International units *in vacuo*, are

$$\begin{cases} 19475{\cdot}2 \\ 19570{\cdot}9 \end{cases} \qquad \begin{cases} 24978{\cdot}3 \\ 25060{\cdot}9 \end{cases} \qquad \begin{cases} 27507{\cdot}0 \\ 27579{\cdot}2 \end{cases} \qquad \begin{cases} 28873{\cdot}1 \\ 28935{\cdot}9 \end{cases}$$

and the separations are respectively 95·7, 82·6, 72·2, 62·8. Fowler has represented the less refrangible components by the formula

$$\nu = 31956{\cdot}22 - 109679{\cdot}22/(m + 0{\cdot}964402)^2, \tag{1}$$

which only gives errors 0·0, 0·7, 1·1, 0·0, and there is no doubt that these components follow the usual laws of series.

The simple Rydberg formula calculated for the other components is

$$\nu = 32014{\cdot}42 - \mathrm{N}/(m + 0{\cdot}968866)^2, \tag{2}$$

with errors 0·0, 9·4, 7·1, 0·0, and is not satisfactory. Fowler has, therefore, added one more constant, and, calculating from the first, second, and fourth lines, obtains

$$\nu = 32005{\cdot}66 - n/(m + 0{\cdot}982328 - 0{\cdot}024835/m)^2, \tag{3}$$

with errors 0·0, 0·0, 2·9, 0·0. This is more satisfactory, but not completely so.

The limiting doublet separations become, in the two cases, 58·2, 49·4, and we are led to the question of a possible further reduction of these separations by formulæ of increasing accuracy.

In order to test this point, we may notice that in a formula

$$\nu = \mathrm{A} - \mathrm{N}/\mathrm{D}_m^2,$$

where D_m proceeds in inverse powers by a series which is not very convergent, a more accurate limit will be obtained by calculations which do not include the first line, in which the divergence is most serious, provided, of course, that all the lines are measured with an equal degree of accuracy. This is the case for the four lines of the present series. Calculating, therefore, from the second, third, and fourth lines and using the better form of the series

$$\mathrm{D}_m = m + \mu + \frac{\alpha}{m + \mu}, \tag{4}$$

obtained in a preceding paper on the line spectrum of helium,* we can obtain the limit more accurately. Since μ is nearly unity,

$$D_m = m+\mu+\frac{\alpha}{m+1} \tag{5}$$

will serve almost equally well. Adopting this form, the calculated limit becomes

$$A = 31992{\cdot}9. \tag{6}$$

This already further reduces the limiting separations by 12·6, and it now becomes 36·7, representing the best value which can be obtained by a formula involving only three lines.

The next step in the demonstration makes use of all the four lines for the calculation of a formula with an extra constant, and of the more appropriate form. The final result of this calculation is

$$\nu = 31982{\cdot}8 - 109679{\cdot}2/D_m^2,$$

where $$D_m = m+1{\cdot}069416 - \frac{0{\cdot}55971}{m+1{\cdot}069416} + \frac{0{\cdot}80624}{(m+1{\cdot}069416)^2}. \tag{7}$$

The limit falls 10 more units, the divergence of the doublets at the limit being now only about 27 units. This is not the most accurate formula which can be obtained from the four lines, and it is not yet very convergent for the earlier lines. It is evident that the next term in D_m will be important in the lines $m = 2, 3$, and, therefore, that the limit is still incorrect. Since every improvement in the formula has led to a marked depression in the limit, which now only differs by about 27 from the value for the companion series, there is every reason to believe that the limits are actually identical, and that the correspondence with line series extends further than the occurrence of the series relation.

The most accurate formula which can be obtained from the four lines is calculated as shown below, and involves a further decrease in the limit. Details of the calculation are given, as it takes the form which appears to be most convenient for general application. Writing the limit of the series as

$$A = 31955{\cdot}9+\delta A,$$

where δA is small, and

$$\nu_m = A - N/\rho_m^2 \qquad (m = 2, 3, \ldots), \tag{8}$$

31955·9 being a more exact limit for the other components with a simpler law, and N being the Rydberg constant, we find for the four lines, on calculation,

$$\left.\begin{aligned} \rho_2 &= 2{\cdot}975883 - 0{\cdot}00012014\,\delta A \\ \rho_3 &= 3{\cdot}988380 - 0{\cdot}00028922\,\delta A \\ \rho_4 &= 5{\cdot}005990 - 0{\cdot}00057189\,\delta A \\ \rho_5 &= 6{\cdot}026428 - 0{\cdot}00099775\,\delta A \end{aligned}\right\}. \tag{9}$$

* 'Roy. Soc. Proc.,' A, vol. 91, p. 255 (1915).

If the four values are fitted into a formula,

$$\rho_m = m+\mu+\frac{\alpha}{m+\mu}+\frac{\beta}{(m+\mu)^2}+\frac{\gamma}{(m+\mu)^3}, \tag{10}$$

known already to be most appropriate to the helium line series, we easily obtain

$$(5+\mu)^3\rho_5-3\,(4+\mu)^3\rho_4+3\,(3+\mu)^3\rho_3-(2+\mu)^3\rho_2 = 24\mu+84, \tag{11}$$

which is a cubic for μ. Neglecting the portions of the ρ's dependent on δA, it becomes

$$-0{\cdot}002285\,\mu^3+0{\cdot}011742\,\mu^2-5{\cdot}532276\,\mu+7{\cdot}405136 = 0, \tag{12}$$

whence $\mu = 1{\cdot}341395$. The correction to this value, dependent on δA, is, if $\delta\rho$ is the corresponding correction for any number ρ, determined by

$$3\,\delta\mu\,\{(5+\mu)^2\rho_5-3\,(4+\mu)^2\rho_4+(3+\mu)^2\rho_3-(2+\mu)^2\rho_2-8\}$$
$$= -\{(5+\mu)^3\delta\rho_5-3\,(4+\mu)^3\delta\rho_4+3\,(3+\mu)^3\delta\rho_3-(2+\mu)^3\delta\rho_2\},$$

and ultimately

$$\mu = 1{\cdot}341395-0{\cdot}01152\,\delta A. \tag{13}$$

With the extreme value of δA which is possible, we can show γ to be so small that for $m = 6$, the term in γ does not contribute a significant amount to ρ_m, and the contribution to ρ_3 is small in comparison with that to ρ_2. A similar calculation to the above, performed with $m = 3, 4, 5, 6$, would therefore give a result very close to that for $m = 3, 4, 5$, only, and the value for (3, 4, 5) combined with that for (2, 3, 4, 5) expressed in (13) will lead to a limit more accurate than even that in (7), although still not exact enough.

The calculation with $m = 3, 4, 5$, proceeds by writing

$$\rho_m = m+\mu+\frac{\alpha}{m+\mu}+\frac{\beta}{(m+\mu)^2},$$

whence $$(5+\mu)^2\rho_5-2\,(4+\mu)^2\rho_4+(3+\mu)^2\rho_3 = 6\mu+24,$$

and the ultimate solution by the preceding method is

$$\mu = 1{\cdot}245914-0{\cdot}006560\,\delta A. \tag{14}$$

Combining the values (13) and (14) for the higher approximation available,

$$\delta A = 19{\cdot}2, \qquad \mu = 1{\cdot}120211. \tag{15}$$

The limit has again decreased by 8 units, and this decrease therefore continues to be systematic as formulæ of increasing accuracy, and of the type necessary in line spectra, are employed. The doublet separation is now only 18·9 at the limit as against the value 49·4 which accords with the best Hicks formula given by Fowler. It is evident, moreover, from a glance at the series below, and a comparison with (7), that it is not yet in any way

absolute, and that if even another line were available for calculation, the limit would again fall. This final series is

$$\nu_m = 31975{\cdot}1 - 109679{\cdot}2/\rho_m^2,$$

where

$$\rho_m = m + 1{\cdot}120211 - \frac{1{\cdot}0211}{m+1{\cdot}120211} + \frac{2{\cdot}2384}{(m+1{\cdot}120211)^2} - \frac{1{\cdot}4974}{(m+1{\cdot}120211)^3}. \tag{16}$$

That δA is certainly much less even than 19·2 can be proved at once. For a calculation from the first three lines gives, by this method,

$$\mu = 1{\cdot}160446 - 0{\cdot}003384\,\delta A. \tag{17}$$

This cannot be so accurate as (14), which again is not so accurate as (13).

Let us suppose that (13), which has the least error, and uses all four lines simultaneously, is correct. Then the errors in (17) and (14) are mainly derived from neglect of the term in γ, and are roughly in the ratio $(4+1)^3/(3+1)^3 = 2$. If, therefore, ϵ is the error in (14), we may write with a close approximation

$$\left.\begin{aligned} \mu &= 1{\cdot}341395 - 0{\cdot}01152\,\delta A \\ &= 1{\cdot}245914 - 0{\cdot}006560\,\delta A + \epsilon \\ &= 1{\cdot}160446 - 0{\cdot}003384\,\delta A + 2\epsilon \end{aligned}\right\} \tag{18}$$

and, solving these three equations,

$$\delta A = 5{\cdot}6.$$

This is the most probable value of δA which can be derived from the four doublets, and it is very conclusive. We can now hardly doubt that the limit is identical with that of the simpler series. On this supposition, the doublet series is analogous to a Principal series in line spectra. Without measurements of further members of the more refrangible components, however, no formula can be given for these members of a much more satisfactory character than (7), and the question of the relation of the constants $\mu, \alpha, \ldots$, to those of known helium series cannot be investigated. The rapid change of these constants with the addition of an extra term to the formula precludes any precise specification of their values at present.

The First Series of Doublets.

The other series of doublets isolated by Fowler has for its leading members the wave numbers given in the Table, where δn denotes the doublet separations, and δn_1, δn_2, their first and second differences.

n.	m.	δn.	δn_1.	δn_2.	n.	m.	δn.	δn_1.	δn_2.
21506·3 21613·7	2	107·4	21·9	11·5	32552·9 32591·6	7	38·7	8·6	0·6
27192·1 27277·6	3	85·5	10·4	−8·2	32920·0 32956·9	8	36·9	1·8	6·8
29785·2 29860·3	4	75·1	18·6	9·4	33185·6 33210·9	9	25·3	11·6	−9·8
31178·6 31235·1	5	56·5	9·2		33379·0 33401·0	10	22·0	3·3	8·3
32014·4 32061·7	6	47·3							

The differences appear to be quite irregular, although there is a remarkable oscillation in the second differences. A study of the values of δn indicates a definite convergence towards zero, but in an irregular manner. This irregularity is exactly of the type which would be expected if the more refrangible components followed a series law of the form

$$\nu = \mathrm{A} - \mathrm{B}/\rho_m^2,$$

where

$$\rho_m = m + \mu + \frac{\alpha}{m+\mu} + \frac{\beta}{(m+\mu)^2} + \ldots,$$

the coefficients α, β, γ,..., not converging rapidly to zero, and being alternately positive and negative, whereas in the corresponding series for the less refrangible components, the convergence of α, β, γ, to zero is rapid. The preliminary series given by Fowler accord with this result. For the less refrangible components, he finds a simple Rydberg formula,

$$\nu = 34295{\cdot}86 - 109679{\cdot}22/(m + 0{\cdot}928427)^2, \tag{20}$$

to be nearly satisfactory, and a corresponding Hicks formula does not show much improvement. It must be borne in mind, of course, that only the first three doublets are measured with great accuracy, although the next three or four must be fairly accurate. The later values are admittedly approximate.

A formula of the proper generalised Rydberg type has been calculated from the first four lines of this simple series, and the result is

$$\nu = 34296{\cdot}1 - \mathrm{B}/\rho_m^2, \tag{21}$$

$$\rho_m = m + 0{\cdot}907876 + \frac{0{\cdot}34020}{m + 0{\cdot}907876} - \frac{1{\cdot}54661}{(m+0{\cdot}907876)^2} + \frac{2{\cdot}12558}{(m+0{\cdot}907876)^3}.$$

The limit is almost exactly that obtained by Fowler from the simpler series,

which he concluded must be nearly correct. But the discrepancies between observed and calculated values given by the simpler formula cannot be removed without using a formula with comparatively large values of α, β, and γ. The difference between the two types of series into which the more and the less refrangible components fall is, therefore, not so pronounced as appears at first sight.

The problem of determining the limit of the more refrangible associated series remains.

The application of the simple Rydberg and the Hicks formulæ by Fowler gives for this series the limits 34330·18, 34324·72, the more accurate formula giving a limit nearer to that of the less refrangible series of components. Fowler has also used a Hicks formula with an extra constant, giving a limit 34310·97, which is again noticeably nearer. But even this formula is by no means satisfactory as a representation of the lines, and the steady decrease which has already taken place in the limit with each improvement in the representation, combined with the results of our examination of the other set of doublets, leaves little doubt that this series of doublets is also of a Principal type, if the calculation is pushed further. For even the apparent limiting separation of the doublets is by no means so large as it was in the first series with which this paper deals. The complete investigation follows so closely along the lines already described for the other doublet series that there is no need to give it in detail here. One or two of its main features may be mentioned.

If the limit of the series is taken as $34296{\cdot}1+\delta A$, the values of ρ_m in

$$\nu = A - B/\rho_m^2$$

are

$$\begin{aligned}
\rho_2 &= 2{\cdot}940786 - 0{\cdot}00011595\,\delta A \\
\rho_3 &= 3{\cdot}953183 - 0{\cdot}00028168\,\delta A \\
\rho_4 &= 4{\cdot}972534 - 0{\cdot}00056069\,\delta A \\
\rho_5 &= 5{\cdot}985934 - 0{\cdot}00097825\,\delta A \\
\rho_6 &= 7{\cdot}006214 - 0{\cdot}00156886\,\delta A \\
\rho_7 &= 8{\cdot}021678 - 0{\cdot}00235516\,\delta A \\
\rho_8 &= 9{\cdot}049840 - 0{\cdot}00338261\,\delta A \\
\rho_9 &= 10{\cdot}053262 - 0{\cdot}00463841\,\delta A
\end{aligned}$$

The last figures are not very reliable beyond ρ_4, and even the last three figures may be incorrect in later entries.

Fowler's Hicks formula was derived from the first, second and seventh lines. The seventh may not be very accurate, and the first should not be used in the problem of merely determining the limit accurately, which is our present purpose.

Applying the Hicks formula to the second, third and fourth lines, as the most suitable and accurate trio, in the form

$$\rho_m = m+\mu+\frac{\alpha}{m} \qquad (m = 2, 3, 4),$$

we find

$$\delta A = 5{\cdot}54.$$

But on the theory of the preceding paper, a better value must be given by

$$\rho_m = m+\mu+\frac{\alpha}{m+\mu} = m+\mu+\frac{\alpha}{m+1}$$

nearly, for μ is evidently close to unity. This leads to $\delta A = 2{\cdot}16$ or very nearly zero. On the supposition, therefore, that the second, third and fourth lines are measured accurately, the limit of the series is almost certainly that of the less refrangible components. Further examination on these lines need not be given, but we may perhaps notice that with $\delta A = 0$ we can deduce a formula with three constants

$$\nu = 34296{\cdot}1 - 109679{\cdot}22/\rho_m^2,$$

$$\rho_m = m+1{\cdot}16802-\frac{1{\cdot}30932}{m+1{\cdot}16802}+\frac{1{\cdot}99441}{(m+1{\cdot}16802)^2},$$

from the first three lines, which is as satisfactory as that calculated by Fowler according to the Hicks model and with a later line. With the same number of constants, more satisfactory formulæ have been obtained throughout when the generalised Rydberg form has been used.

Summary.

1. The paper gives further support to Fowler's conclusion that the heads of the bands in the band spectrum of Goldstein and Curtis follow ordinary line-series laws, by showing that the doublet separations tend to zero at the limits of the series.

2. Both the doublet series isolated by Fowler are strictly analogous to Principal series in line spectra.

3. The generalised Rydberg formula gives the most suitable representation of these series as well as of line series.